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X-ray Absorption Near Edge Structure of FePt nanoclusters

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Abstract

X-ray Absorption Near Edge Structure [XANES] of FePt nanoclusters has been studied using a full multiple scattering, self-consistent field [SCF], real-space Green's function approach realized via the powerful ab initio FEFF8 code. One purpose of our study is to determine the sensitivity of Pt L3 edge with respect to the size and shape of the FePt nanoclusters. We also give the results of the calculations with respect to the Fe L3 edge. Calculations are made with and without core-hole for two main reasons, to check and cross-check the FEFF code and also since in some cases it is known such as Pt clusters that better results are obtained without the core-hole. This is mainly because the screening electron will occupy empty d or f states and correspondingly reduce the white line intensity.

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1 Introduction

In a previous note [1] we have reported on the temperature dependent polarized X-ray absorption near-edge structure [XANES] spectra measured at the beamline BL13-B1 [Photon Factory, KEK], in the fluorescence mode from 10K to 300 K for a very good quality single crystal of LSCO co-doped with 1% Zn at the copper site. The main focus of [1] was experimental, although some initial results of the theoretical spectra generated by FEFF8.10 [5], by using default settings [by intention] were given. In this note we continue our quest of using the FEFF code to study systems of interest to us. In this short note we consider small FePt clusters at both Pt and Fe L3 edges. The FePt clusters are not only of academic interest due to their applications to catalysis and useful magnetic properties i.e. for ultrahigh density magnetic data storage media [2]. The sensitivity of Pt x-ray absorption near edge structure to small Pt clusters has been recently given by [3].

Thus the purpose of this note is to concentrate on the theoretical calculation using the updated version of FEFF8, i.e. FEFF8.20 [4]. Here we report on our results of small FePt clusters, giving the difference $\mu(E)$ spectra between clusters and the appropriate bulk and between clusters at both the Pt and Fe L3 edges. In addition to unpolarized spectra, we include the results taking polarization into account. Another aim is to provide a concrete example of the application of XANES and DOS calculations using FEFF. Indeed, although FEFF is a powerful code, its self-consistency must be demonstrated by applications to real systems systematically. Moreover by actual calculations one can illustrate advantages and disadvantages, and thus find ways of improving the code.

The set-up of this paper is as follows, in the next section we outline some brief remarks about Electron Multiple Scattering using FEFF. Section three deals with results and discussion and finally we state the conclusions.

2 Electron Multiple Scattering using FEFF

In this note we concentrate on giving the difference $\mu(E)$ spectra. The value $\mu(E)$ is the main quantity in XANES. Here we look at the basic definitions restricting ourselves to brief comments. As is well-known the primary quantities with which XANES calculations are concerned are μ, μ_0, χ , and $\rho_{li}(E)$ [5]

$$\mu_{li}(E) = \mu_{li}^{0'}(E)[1 + \chi_{li}'(E)]. \quad (1)$$

We note that the prime is here for clarity since it reminds us that it denotes final state quantities in the *in the presence of screened hole*. The central quantity in X-ray Absorption Spectroscopy [XAS] is the absorption coefficient $\mu(E)$. As is known there is a close and deep connection between XAS and *electronic structure*, which is indicated and implied by the resemblance of the contribution from a site, i and orbital angular momentum l and the local l -projected electronic density of states [LDOS] at site i

$$\rho_{li}(E) = \rho_{li}^{0'}(E)[1 + \chi_{li}(E)]. \quad (2)$$

However it is important to bear in mind that since core hole plays a significant role in calculation of XAS, the similarity between XAS and LDOS cannot be regarded as an absolute.

It is important to keep in mind that FEFF method starts from the most fundamental quantity i.e. the Real Space Green's Function and constructs the physical quantities of interest from it [5, 4]. This is one of the code's main attraction since unlike band calculations it does not depend on symmetry. In this sense it is ideal for cluster physics².

3 Results and Discussion

Let us now give the results and analysis of our calculated theoretical results obtained with FEFF8.2, and the difference spectra extracted with athena [version 0.8.024][6]. For the background definitions and formalism of FEFF8.2 we refer to its main reference [4]. We note that the Pt L3 edge roughly lies at 11,564 eV and the Fe L3 is located at approximately 706.8 eV. In this note we consider only the L3 edges of Pt and Fe. We studied both nearly spherical [i.e.cuboctahedral] clusters and small non-spherical clusters with 3, 4, 5, and 8 atoms [3]. The results of the nearly spherical clusters will not be discussed here. Suffice is to say that we have used a spherical cluster of 55 atoms as a definition of bulk for Pt L3 edge, it has 1 central atom, 12 atoms in first shell, 6 in the second shell, 24 in third shell, and the remaining in the fourth shell. For the Fe L3 edge we have used a 65 atoms clusters as defining the bulk. The 3 atoms planar cluster is written as (3,1) in the notation of Bigot and Minot[7], for 4 atoms we can have the pyramid (4,1) and planar rhombus configuration (4,2), the 5 atoms allows again 2 possibilities, the square pyramid (5,2) and trigonal bi-pyramid (5,4). Finally for the 8 atoms cluster we have three configurations bi-capped octahedron (8,8), capped D5h bi-pyramid (8,2,1) and trigonal prism with 2 square faces capped (8,2,4).

Fig. 1 displays the XANES difference spectra of the FePt 8 [xmu824] atom cluster with respect to the bulk PtFe at the Pt L3 edge as a function of the energy. This data is for the unpolarized case. The spectrum in Fig.1 clearly shows that we can see the difference from the bulk at the L3 Pt edge, for the case of this FePt cluster. We have likewise calculated the difference spectra with respect to the bulk for other clusters and find significant deviations from the bulk. Next we turn to the polarized case, see Fig. 2. For illustration the polarized result is given for another 8 atom cluster i.e. xmu821 cluster. The deviation from the bulk is again significant. We note here that the polarized difference spectra do not vary significantly from the corresponding unpolarized case, but the variation is significant between the polarized and unpolarized case when the morphology is different, although the number of atoms is the same, as is clear by comparing Figs. 1 and 2.

The results for the Fe L3 edge for both the unpolarized and the polarized case are given in Figs. 3 and 4 respectively.

²It is known that XANES and EXAFS signals are sensitive to local structure. Indeed just as XRD is indicative of long-range order, XANES and EXAFS carry signatures of short range order or disorder.

Finally we consider the difference spectra between clusters of same morphology and same number of atoms, but with different atom species. To this end we take the difference spectra of FePt cluster and a pure Pt cluster. The unpolarized case is shown in Fig. 5 at the Pt L3 edge as a function of the energy, for the morphology (8,2,4). Likewise the polarized case is indicated in Fig. 6 for the morphology (8,8).

Several results are not shown here in this short presentation. Interesting results are obtained if we take the difference of polarized spectrum with respect to the corresponding unpolarized case, in this instance one gets the “polarization dichroic” signal [3] which depends strongly on the shape of the cluster. It is interesting to note that as intuitively expected the effect of polarization should be minimal for the nearly spherical clusters. We find this to be the case, thus providing a check on our calculations.

It is worth noting that the calculations were carried out with and without core-hole for two main reasons, to check and cross-check the FEFF code and also since in some cases it is known such as Pt clusters that better results are obtained without the core-hole. This is since the screening electron occupies empty d or f states and correspondingly reduces the white line intensity.

4 Conclusions

The results and the analysis of the XANES of FePt nanoclusters using a full multiple scattering, self-consistent field SCF, real-space Green’s function approach realized via the powerful ab initio FEFF8 code have been outlined here. One purpose of our study was to determine the sensitivity of Pt L3 edge with respect to the size and shape of the FePt nanoclusters, another was to give the results of the calculations with respect to the Fe L3 edge. These points have been demonstrated. Moreover results have also been given when polarization is considered. In summary the XANES spectrum shows sensitivity to the cluster size, morphology, and polarization at the Pt and Fe L3 edge, for FePt clusters.

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Figure 1: The difference χ_{mu} spectra of the (8,2,4) FePt cluster with respect to the bulk PtFe at the Pt L3 edge, is plotted against energy. This unpolarized XANES data is generated with FEFF8.2.

Figure 2: The difference χ_{mu} spectra of the (8,2,1) FePt cluster with respect to the corresponding bulk FePt at the Pt L3 edge. In this case polarization is included.

Figure 3: The difference χ_{mu} spectra of the (8,8) FePt cluster with respect to the bulk FePt at the Fe L3 edge, is plotted against energy.

Figure 4: The difference χ_{mu} spectra of the (8,2,1) FePt cluster with respect to the bulk FePt at the Fe L3 edge. Polarization is included.

Figure 5: The difference χ_{mu} spectra of the (8,2,4) FePt cluster with respect to the (8,2,4) Pt cluster at the Pt L3 edge.

Figure 6: The difference χ_{mu} spectra of the (8,8) FePt cluster with respect to the (8,8) Pt cluster at the Pt L3 edge when the polarization is taken into account.











